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(54) Title: METHOD FOR DELIVERING CHEMICALS TO AN OIL OR GAS WELL

(57) Abstract: A method of delivering chemicals to well such as an oil or gas well, the method comprising encapsulating the chemicals in or on a carrier particle such as starch, and delivering the carrier-encapsulated chemical to the well.

METHOD FOR DELIVERING CHEMICALS TO AN OIL OR GAS WELL

This invention relates to a method for encapsulating chemicals and particularly to a method for starch and wax encapsulation of aggressive chemicals for applications in the oil industry. The invention relates especially to a method of delivering chemicals to an oil or gas well, in encapsulated form.

Advances in drilling and completion technology have revolutionized new field development and the use of sub-sea wells with long tiebacks is now common. The low temperatures and long fluid transport times under sub-sea conditions often result in a wide variety of production chemistry related problems, including corrosion, scale, wax and asphaltene deposition, hydrate formation, bacterial growth and the transport of viscous fluids including emulsions. The control of these problems is usually achieved by continuous chemical injection at the sub-sea well head along separate, multiple injection lines.

The installation of multiple chemical injection lines is extremely expensive both for subsea wellhead and continuous downhole injection, especially in deepwater environments.

A deployment method which allowed a reduction in the number of chemical injection lines required to deliver the cocktail of chemicals required at each wellhead would offer significant cost benefits.

The deployment of combined chemical treatment packages, for example scale and corrosion inhibitors, has been considered as one method of reducing the number of chemical injection lines. This has been achieved on a limited commercial basis by blending selected oilfield chemicals together to form a compatible mixture. However, the development of combined chemical packages is fraught with difficulties due to compatibility issues and is limited to a small range of products and product types. This limits the types of combined treatment available and depending upon the nature of the problem often still results in the use of several injection lines.

According to the present invention there is provided a method of delivering a chemical to an oil or gas well, the method comprising associating the chemical with a carrier, and delivering the chemical plus carrier to the well.

The chemical can be encapsulated by the carrier or otherwise entrapped by the carrier. The carrier preferably comprises a suspension or slurry of particles onto or into which the chemical can be loaded. A typical carrier is particulate starch, but other good carriers can be encapsulating agents conventionally known from e.g. the food, paint and pharmaceutical industries, such as gum arabic, waxes, PVOH, polylactic acids, dextrins, low viscosity modified starches, arabinogalactan, gum acacia, casein, gelatin, carboxymethylcellulose, tragacanth, karaya, sodium alginate, tannin, and celluloses.

We have found that deploying the chemicals on or in a slurry of nano/micro particles can alleviate compatibility issues during storage and deployment and thus facilitate the injection of multiple chemicals via a single chemical injection line. The nano/micro particles can typically contain a high active level of oilfield chemical, typically 5-90%v/v, and can be dispersed in either an aqueous or oleic medium, and in solution or suspension, depending upon the nature of the encapsulation matrix. The entrapped oilfield chemicals are typically released upon contact with the produced fluids due to the breakdown of the coating or carrier matrix either thermally and/or as a result of mixing with oil or water. The potential to control the rate and extent of release as a function of time can also allow chemicals to be transported and released along different sections of the

pipeline, thus alleviating some of the kinetic problems associated with scale, wax and hydrate inhibitors in long subsea tie backs.

This can enable the simultaneous delivery of combined oilfield chemical packages to platform, remote and complex wells through a single injection line. The oilfield production chemical-entrapped particles could be injected topsides, at sub sea wellheads or elsewhere in the well. The particles could also be applied to deliver oilfield chemicals that cannot be effectively deployed by conventional solvents. Certain embodiments may include the delivery of a single oilfield chemical to a well while associated with a carrier such as the above-mentioned compounds.

The chemical is typically injected continuously into the well, typically through a dedicated fluid line.

The nano/micro particle entrapment technology can be applied to deliver a wide range and a wide combination of oilfield production chemicals down one injection line or umbilical. This includes, but is not limited to scale inhibitors, corrosion inhibitors, wax inhibitors, asphaltene inhibitors, hydrate inhibitors, oxygen scavengers, hydrogen sulphide scavengers, demulsifiers, biocides, gel breakers, tracers, friction reducers, surfactants, de-oilers and antifoaming agents. The oilfield chemicals can be entrapped in either liquid or solid form.

The particles can be manufactured using a variety of techniques including complex coacervation, interfacial polymerisation, desolvation, extrusion, agglomeration, emulsion polymerisation, gelation, chemical vapour deposition, fluid bed coating, spray drying and combinations thereof. The particles can be produced over a variable particle size, typically, 1nm–850μm and can contain a high active level of oilfield chemical, typically 1-90%v/v. Nano/micro particles containing different oilfield production chemicals can be dispersed into either an aqueous or oleic carrier fluid, that may or may not contain other oilfield production chemicals, using either ionic or non-ionic surface active agents. The material is preferably stable under injection conditions in both aqueous and non-aqueous environments at the ambient and sub-ambient temperatures that may be encountered in a production environment. The entrapped oilfield chemical can be rapidly released from the encapsulating and/or carrier medium as a result of either thermal degradation of the matrix and/or dissolution in either the oil or water phase, releasing the oilfield chemical under wellhead conditions. The release time of the chemical upon contact with the produced fluids could also be delayed depending upon the nature of the entrapment matrix. This can allow chemicals to be transported and released along different sections of the pipeline, thus enabling the release of chemicals in the right place and alleviating some of the kinetic problems associated

with scale, wax and hydrate inhibitors in long sub sea tie backs.

The entrapment of certain oilfield chemicals could reduce the corrosivity of the fluid to be deployed into the wellhead or downhole injection system. This could permit the umbilicals and downhole injection lines to be fabricated from lower cost carbon steels rather than the more expensive stainless steels and/or corrosion resistant alloys.

The particles containing different production chemicals, in either solid or liquid form, can then be mixed together to produce the required blend of oilfield chemicals for dispersion into the fluid carrying medium which may be aqueous or organic based. The solid particles could be dispersed into the fluid-carrying medium by use of a wide range of different types of amphoteric, anionic, cationic and nonionic surface-active agents. Amphoteric surfactants could include acetates such as lauro-, alkyl- and coco-amphoacetates, betaines such as lauryl-, alkyl- and coco-amidopropylbetaines, glycinates, imidazolines and propionates such as lauro-, alkyl- and coco-aminodipropionate. Anionic surfactants could include alkyl- alkylaryl-, alkylether and alkylarylether sulphonates and carbonates, lignin derivatives, olefine and paraffin sulphonates, phosphate esters and sarcosinates. Cationic surfactants could include amides, amines, amidoamines, diamines and quaternaries such as didecyldimethylammonium. Nonionic surfactants could

include alkoxylates such as alcohol-, alkylphenol-, amide-, ester-, fatty acid- and glyceride ethoxylates, alkylamides, amine oxides and esters.

The required dispersing characteristics could be achieved for example by varying the ratio of a sorbitan ester and a sorbitan ester ethoxylate to achieve the desired hydrophilic - lipophilic balance (HLB).

The chemical is typically coated or otherwise associated with a carrier such as starch, flour or wax. The starch can decompose at a given temperature releasing the chemical at a second location where it is needed. Selection of the characteristics of the carrier (e.g. starch) used allows accurate control over the temperature of decomposition. Normally the temperature at the wellhead will be hotter than the surface of the well. The precise temperature at the wellhead will vary from well to well, and typical subsea wellheads may have an ambient temperature of around 110°C (compared with 20°C at surface). The starch or wax coat can typically be designed to decompose when it crosses a point on the temperature gradient and so release the chemicals. In particular, wax carriers can be designed to degrade or dissolve slowly or after a set time has elapsed to release the chemicals continuously over a period of time or after a set interval e.g. in the production fluids. The starch or wax may be modified to decompose at different temperatures as may be necessary for

particularly shallow or particularly deep wells or for any other reason in which the temperature of the wellhead may be different from normal. The starch is typically granular starch, and resistant starch made therefrom. The chemical is typically adsorbed onto the starch, typically by simple mixing. Adjuncts useful in controlled release formulations can be added.

All granular starches and flours (hereinafter "starch") may be suitable for use herein and may be derived from any native source. A native starch as used herein, is one as it is found in nature. Also suitable are starches derived from a plant obtained by standard breeding techniques including crossbreeding, translocation, inversion, transformation or any other method of gene or chromosome engineering to include variations thereof. In addition, starch derived from a plant grown from artificial mutations and variations of the above genetic composition, which may be produced by known standard methods of mutation breeding, are also suitable herein.

Typical sources for the starches are cereals, tubers, roots, legumes and fruits. The native source can be corn, pea, potato, sweet potato, banana, barley, wheat, rice, sago, amaranth, tapioca, arrowroot, canna, sorghum, and waxy or high amylose varieties thereof. As used herein, the term "waxy" is intended to include a starch containing at least about 95% by weight amylopectin and the term

"high amylose" is intended to include a starch containing at least about 40% by weight amylose.

Conversion products which retain their granular structure may be derived from any of the starches, including fluidity or thin-boiling starches prepared by oxidation, enzyme conversion, acid hydrolysis, heat and or acid dextrinization, and or sheared products may also be useful herein.

Particularly useful are granular structures, which have been "pitted" by the action of enzymes or acid, leaving a still organised structure that creates a microporous starch. The enzymatic or acid hydrolysis of the starch granule is carried out using techniques well known in the art. The amount of enzyme used is dependent upon the enzyme, i.e., type, source and activity, as well as enzyme concentration, substrate concentration, pH, temperature, the presence or absence of inhibitors, and the degree and type of modification. Types of modifications are described herein, *infra*. These parameters may be adjusted to optimise the nature and extent of the "pitting" of the starch granule.

Another particulate starch useful in the controlled release applications of the present invention is resistant starch. Resistant starch is commonly known as a starch not likely to be adsorbed in the small intestine of a healthy individual. Granular or particulate starches, such as of the RS2-type (a starch granule that resists digestion by pancreatic

alpha-amylase) and the RS4-type (a chemically modified starch, such as acetylated, hydroxyalkylated, or cross-linked starch) are particularly suitable. However, resistant starches of the RS3-type (retrograded, non-granular starch formed by heat/moisture treatment of starch) are also suitable for the instant invention due to their high level of retrogradation or crystallisation from the alignment and association of associated amylose.

These types of resistant starch are well known in the art and may be exemplified by that disclosed in US Patent Nos. US 5,593,503 which describes a method of making a granular resistant starch; US Patent Nos. 5,281,276 and 5,409,542 which describe methods of making resistant starches of the RS3 type; US 5,855,946 which describes a method of making a resistant starch of the RS4-type; and U.S. Application Serial No. 60/157370, which describes the formation of a very highly resistant starch. The methods for making the resistant starches are described in the preceding references, the disclosures of which are incorporated herein by reference.

The starch particulate, including granular and resistant starches, may be modified by treatment with any reagent or combination of reagents that contribute to the controlled release properties of the starch.

Chemical modifications are intended to include crosslinked starches, including crosslinking the particulate starch with reactive polymers. Preferred reactive polymers include starches modified with aldehyde or silanol groups. Other chemical modifications include, without limit, acetylated and organically esterified starches, hydroxyethylated and hydroxypropylated starches, phosphorylated and inorganically esterified starches, cationic, anionic, non-ionic, and zwitterionic starches, and succinate and substituted succinate derivatives of starch.

Preferred modified starches are starch acetates having a degree of substitution ("DS") of about up to about 1.5, particularly those disclosed in US 5,321,132, thereby improving compatibility with synthetic hydrophobic materials. Such modifications are known in the art, for example in Modified Starches: Properties and Uses, Ed. Wurzburg, CRC Press, Inc., Florida (1986).

Other suitable modifications and methods for producing particulate starches are known in the art and disclosed in U.S. Patent No. 4,626,288 which is incorporated herein by reference. In a particularly useful embodiment, the starch is derivatized by reaction with an alkenyl cyclic dicarboxylic acid anhydride by the method disclosed in U.S. Patent Nos. 2,613,206 and 2,661,349, incorporated herein by reference, or propylene oxide, more particularly by reaction with octenylsuccinic anhydride.

The encapsulated chemicals can be carried in a liquid-phase inhibitor or other chemical to be delivered to the well that may be incompatible with the encapsulated chemical. All chemicals to be delivered could then be injected through a single umbilical. Two umbilicals could be installed to allow operations to continue in the event of one blocking up. Additionally a third umbilical for methanol could be provided. A total of three umbilicals could therefore provide adequate cover for a well. This represents a significant saving when compared with the prior art, which requires five or six umbilicals for comparable performance.

Embodiments of the present invention will now be described by way of example with reference to the following examples.

Example 1: Encapsulation of solid material

US Patent 4755397 to Eden et al (incorporated herein by reference) describes a process for the starch encapsulation of a solid material, namely, ferric hydroxide, which can be adapted for the encapsulation of oilfield chemicals as follows.

The desired oilfield chemical is dissolved in acidified water, dilute sodium hydroxide is added as necessary while stirring to remove from the chemical any trace precipitates. Ammonium sulphate, water and high amylose (70%) cornstarch is added to the chemical slurry to give a slurry of the following composition:

Starch	410 grams	(19.9%)
Ammonium sulphate	610 grams	(29.6%)
Chemical	41 grams	(2.0%)
Water	1000 grams	(48.5%)

This slurry is processed through a jet cooker (Model C-1, National Starch & Chemical Corp) at 150°C. At this temperature the high amylose starch cooks, despite the presence of a high level of an inhibiting salt, and forms a uniform dispersion. A ball valve attached to the outlet of the jet cooker can be adjusted so that a pressure drop from maximum cooking temperature and pressure to atmospheric pressure occurs as the starch cook passes through the valve. Upstream the pressure is typically 90psig; downstream the pressure is typically 0psig.

As the starch passes through the valve and the pressure is reduced to atmospheric, its temperature drops to around 104°C, the boiling point of the salt solution at atmospheric pressure. At this temperature, the starch precipitates essentially instantaneously entrapping the solid oilfield chemical. The product collected at the cooker outlet is typically a slurry of tan particles 5 to 7 microns in diameter. The slurry, by volume, is a third salt solution and two thirds precipitated particles. This product is washed free of salt and dried.

The dried particles (40% by weight) containing the various oilfield chemicals are then mixed with a synthetic white oil such as Isopar M (52% by weight)

and a polyalkoxylated alkyl phenol based dispersant (5% by weight) using a high shear, UltraTurrax mixer at 5000 rpm for 10 minutes. A clay based thickening agent (3% by weight) is then added to this mix and blended using a high shear, UltraTurrax mixer at 10,000 rpm.

This process can be used for the production of encapsulated particles containing a)solid biocides; b) de-oilers; c)demulsifiers; d)scale inhibitors; e)corrosion inhibitors; f)wax inhibitors; and g)asphaltene inhibitors. The chemical-loaded particles are mixed in various combinations of chemicals and delivered through a single fluid delivery pipeline to a wellhead, where the temperature of around 110°C breaks down the starch particles and releases the chemicals. Optionally a liquid chemical such as a corrosion inhibitor is mixed with the carrier fluid conveying the particles to the well.

Example 2: Encapsulation of an Active Ingredient
WO9901214 to Fester et al (incorporated herein by reference) describes a process for the encapsulation of an active ingredient, namely, solids and water-soluble fluids. This can be adapted for encapsulation of oilfield chemicals as follows.

Fifteen grams of PN (native potato starch) are added to 100ml water in which 2.5 g Tween 80 is dissolved. Four grams TSTP are dissolved in this suspension, followed by the addition of 20 g of salad oil. An

emulsion forms with the aid of an Ultra-Turrax. The o/w emulsion is then emulsified in a second hydrophobic phase, namely 200ml of paraffin oil. A top stirrer at a speed of 600 rpm is used for this purpose.

A solution of 0.65g NaOH in 10ml water is subsequently added to the emulsion with stirring, in order to initiate partial gelation and cross-linking. After 30 minutes, the stirrer speed is increased to 1000 rpm. After 4 hours the emulsion is broken by addition of acetic acid.

The starch particles collected in the water/acetic acid phase. After separation, the particles are washed with de-ionised water and stored. Examination of the dispersed fluid by light microscopy should indicate that the particles are essentially mono dispersed with a size of 25 μm containing droplets of oil.

This process can be used for the production of encapsulated particles containing solid and/or liquid chemicals, namely, scale and corrosion inhibitors, oxygen and hydrogen sulphide scavengers, demulsifiers, gel breakers, tracers and antifoaming agents. However, the process could be applicable to any solid or water-soluble chemicals. As before the particulate- entrapped chemicals are mixed in various combinations of chemicals and delivered through a single fluid delivery pipeline to a wellhead, where the temperature of around 110°C

breaks down the starch particles and releases the chemicals. Again the liquid phase of the carrier fluid can incorporate a further chemical to be delivered to the well.

Example 3: Encapsulation of a Water Insoluble Liquid

US Patent 4755397 to Eden et al (incorporated herein by reference) describes a process for the starch encapsulation of a water insoluble liquid, namely, peppermint oil, and this can be adapted for the production of starch encapsulation of hydrophobic oilfield chemicals as follows.

A slurry is made of the following composition:

High Amylose (70%Corn Starch)	20%
Ammonium Sulphate	40%
Water	40%

The following is mixed, to disperse the hydrophobic oilfield chemical and added, with mixing, to the previous slurry:

Oilfield chemical	2-10%
Surfactants	90-98%

The resulting slurry/coarse emulsion is jet-cooked through a C-1 cooker as in Example 1. In this case, the cooker outlet hose empties below the surface of a slurry of ammonium sulphate and ice in saturated ammonium sulphate solution (-8°C.) to condense and trap any free peppermint oil vapours. The resulting product is typically coarse (<20 mesh) light tan

powder in salt solution. The powder is recovered by filtration and dried.

A 3% weight aqueous solution of HEC is then prepared by slowly adding the powdered HEC to distilled water and gradually increasing the mixing speed over a five-minute period. Once a solution is formed a sorbitan ester ethoxylate based dispersant (6% by weight) is added to the aqueous HEC mixture and blended at 2000rpm for five minutes. The dried particles (50% by weight) containing the various oilfield chemicals are then mixed with the aqueous solution of HEC and dispersant using a high shear, UltraTurrax mixer at 5000 rpm for 10 minutes.

This process is particularly useful for manufacturing encapsulated products containing oil soluble scale and corrosion inhibitors, wax and asphaltene inhibitors, drag reducers, demulsifiers and de-oilers. A variety of these chemicals can be encapsulated as described above and delivered to a wellhead via a single injection line in various combinations, without interaction between the chemicals in the line during delivery. Upon arrival at the wellhead the starch capsules surrounding the chemicals are broken down by the ambient temperature at the wellhead, and the chemicals are released and activated in situ. Incorporation of incompatible liquid phase chemicals in the carrier fluid does not affect the encapsulated chemical.

Example 4: Encapsulation of a solid or oil soluble product.

US Patent 4997659 to Yatka et al (incorporated herein by reference) describes a process for the encapsulation of a powdered sweetener, namely, Alitame in paraffin and/or microcrystalline wax. This was adapted for the encapsulation of various solid oilfield chemicals as listed above.

A 20% paraffin or micro-crystalline wax, of defined melting point/80% solid oilfield chemical is prepared by mixing the molten wax with the solid chemical, cooling to form an agglomerate and grinding up the agglomerate to form granules. These granules are optionally further processed to form spheres, using a spheroniser. The size of the spheres is controlled by the granulation process but is typically 1-50μm in diameter.

This process is typically used to produce paraffin or microcrystalline wax-based particles containing solid oilfield production chemicals such as scale, wax and corrosion inhibitors, biocides and other scavengers. In addition the wax particles can be manufactured to entrap oil-based liquids such as corrosion, wax and asphaltene inhibitors, demulsifiers and de-oilers.

The nano/micro particles containing different production chemicals, in either solid or liquid form, are dispersed together to produce the required blend of oilfield chemicals for dispersion into the

fluid carrying medium which was either aqueous or organic based. The solid particles are dispersed into the fluid-carrying medium by use of a wide range of different dispersants. Suitable dispersants include fatty acid esters and alkoxylated (e.g. methoxylated or ethoxylated) fatty acid esters such as sorbitan ester and sorbitan ester ethoxylate; and PEG esters such as PEG laurate. By varying the ratio of the ethoxylated sorbitan ester to the sorbitan ester the desired HLB can be obtained.

The encapsulated oil field chemicals are mixed in the desired proportions and delivered via a single fluid delivery line to a wellhead, at which point the wax capsules degrade, releasing the chemical into the wellhead environment. Optionally the two or more chemicals that are delivered to the well can be encapsulated by different methods e.g. according to any of the examples herein, so that the different particles release their chemical burdens at different points in the well, in response to different stimuli.

Example 5: Encapsulation of a wax inhibitor by starch.

A granular starch (150g, starch octenylsuccinate, aluminum salt, commercially available from National Starch and Chemical Company) was added to a wax inhibitor XPC 3147C (50 g, Aldrich) which had been melted at a temperature greater than 30°C. The mixture was stirred at ambient temperature and

pressure in a high shear disperser (Torrence, #785049) at 2000-4000 rpm. An additional 100 g of the granular starch was added to the mixture and stirred for two more minutes to form a fine, free-flowing powder. This is conveyed to a wellhead as previously described through a single fluid line by a carrier fluid that incorporates a scale inhibitor that is incompatible with the wax inhibitor, without any reaction between the chemicals. The scale inhibitor treats the fluid conduit continuously from the point of entry to the wellhead, and the wax inhibitor is activated only after a longer period of time as a result of the starch encapsulating matrix dissolving in the produced fluids.

Example 6: Encapsulation of a water-soluble chemical by starch.

Water-soluble solids were formulated with starch at a 1:1 ratio (50% loading on starch). The oil well chemical was solubilised in ambient water and homogenised for 1-2 minutes at 9000-10000 rpm (Silverson L4RT). The starch was then added to the solution and the mixture was further homogenised for 2-3 minutes at 9000-10000rpm, 20°C (Silverson L4RT). The mixture was spray dried (40% solids, 375°F inlet temperature, 225°F outlet temperature with a feed rate of 160ml/minutes and dual wheel atomisation using Bowen Lab Model (30″ x 36″) to produce a flowable, non-sticky composition.

a. The example was carried out using a scale inhibitor, Scaletreat 2001-28, as the oil well

chemical and Vulca 90, a maize starch crosslinked with 1.5% epichlorohydrin on dry starch.

b. The example was carried out using a corrosion inhibitor, Corrtreat 2001-29 as the oil well chemical and a starch acetate (1.5 DS) waxy maize starch.

c. The example was carried out using a scale inhibitor, Scaletreat 2001-26 as the oil well chemical and a microporous waxy maize starch that was digested using 0.3% glucoamylase on dry starch to achieve 15% digestion.

In each case, the encapsulated chemicals are mixed as desired and delivered in mixtures of encapsulated particles to the well-head through a single fluid line. The encapsulated particles are degraded by the fluid conditions at the well-head, and/or by temperature, thereby delivering their active reagents at the required position in the wellhead.

Example 7: Encapsulation of a water insoluble chemical by starch.

Water insoluble solids were formulated with starch at a 1:1 ratio (50% loading on starch). The oil well chemical was added to a waxy maize starch modified with 3% octenyl succinic anhydride and converted to a water fluidity of 40, and the mixture was homogenised for 1-2 minutes at 9000-10000 rpm, 20°C (Silverson L4RT). Water was added to the emulsion and the mixture was further homogenised, 1 minute at 9000-10000 rpm, 20°C (Silverson L4RT).

The starch was then added to the solution and the mixture was further homogenised, 1-2 minutes at 9000-10000 rpm, 20°C (Silverson L4RT). The mixture was spray dried (35% solids, 380°F inlet temperature, 230°F outlet temperature, 140-160ml/minutes with dual wheel atomisation using Bowen Lab Model (30″ x 36″)) to produce a flowable, non-sticky composition.

a. The example was carried out using a wax inhibitor, Waxtreat 398 as the oil well chemical and a microporous waxy maize which was 30% digested with 0.3% glucoamylase, and modified with 3% octenyl succinic anhydride and crosslinked with 1% aluminium sulphate.
b. The example was carried out using an asphaltene dispersant, Waxtreat 7302 as the oil well chemical and a microporous waxy maize starch modified using 3% octenyl succinic anhydride, enzymatically treated using 0.3% glucoamylase, to achieve 30% digestion.
c. The example was carried out using a hydrogen sulphide scavenger, Scavtreat 1020 as the oil well chemical and a high amylose corn starch, HYLON® VII starch, commercially available from National Starch and Chemical Company.
d. The example was carried out using a kinetic hydrate inhibitor, Hytreat 569 as the oil well chemical and a microporous (30% enzyme digested) waxy maize starch modified using 3% octenyl succinic anhydride, enzymatically treated using 0.3% glucoamylase.

e. The example was carried out using an anti-agglomerate hydrate inhibitor, Hytreat A560 as the oil well chemical and a cationic starch silanol, 0.3% Nitrogen, 0.4% silanol.

Chemicals are delivered through a single delivery line to a wellhead and also to a well bore and formation. The wellhead chemicals are released from their encapsulated particles at the prevailing wellhead conditions and the formation chemicals are only released upon reaching the more aggressive prevailing conditions at the formation.

Example 8

Starch was weighed out into a glass container. The oil well chemical was added while mixing for 5 minutes and then mixed for an additional 5 minutes, or until uniform using a Powerstat, Variable Autotransformer set at 80 (3PN168), Bodine Electric Co, Speed reducer motor (NSE-12R).

a. Starch used was a 50:50 blend of sago and tapioca, DD and the oil well chemical used was Waxtreat 398. The starch:chemical ratio used was 100:40 and the loading was 28.6%.
b. Starch used was a high amylose (70%) maize starch modified by 3% octenyl succinic anhydride and 10% polyvinyl alcohol and the oil well chemical used was Waxtreat 398. The starch:chemical ratio used was 100:80 and the loading was 44.4%.
c. Starch used was enzyme converted (alpha amylase) maltodextrin and the oil well chemical used was

Trosquat. The starch:chemical ratio used was 100:38 and the loading was 27.5%.

d. Starch used was enzyme converted (alpha amylase) maltodextrin and the oil well chemical used was Trosquat. The starch:chemical ratio used was 100:38 and the loading was 27.5%.

e. Starch used was a high amylose (70%) maize that was gelatinised, completely enzymatically de-branched and retrograded and the oil well chemical used was Hytreat A560. The starch:chemical ratio used was 100:24 and the loading was 19.3%.

The encapsulated chemicals are mixed as desired and delivered to production tubing or other well tubulars through a single fluid line. Once reaching the target in the well the chemicals are released through reaction to local conditions.

The wellhead is the preferred target of the chemicals delivered in order to protect the tie backs etc from corrosion or blockage, but it will be appreciated that the present invention is not in any way limited to the delivery of chemicals to the wellhead, and in certain embodiments the delivery target is another portion of the well, such as the formation, the reservoir, the casing, production tubing or other tubular or conduit.

Typical embodiments of the invention mitigate compatibility problems with delivery of mixtures of chemicals to platforms, remote and complex wells

through a single injection line. Some embodiments also facilitate the deployment of certain chemicals that are difficult to handle, for example, because they are very corrosive and/or are insoluble in conventional solvents; for example, polyacrylate wax inhibitors, either alone or in combination with other chemicals, where the chemicals or at least one of them cannot be effectively deployed by conventional solvents.

Certain embodiments also enable the deployment of oilfield chemicals at high active concentrations, for example, ethylene vinyl acetate (EVA) wax inhibitors that cannot be effectively deployed at >10%v/v by conventional solvents.

While starch is a preferred entrapping or coating medium a range of other materials could be used such as natural gums, cellulose and derivatives, polysaccharides, gelatin, wax, fatty acids, acrylic, carboxyvinyl polymers, polyester, polystyrene, polycaprolactone, polyvinyl acetate, polyamides, polyvinyl alcohol, polylactic acid, polyglycolide, shellac, zein, oil based gels, silica gel and other materials consisting of mixtures, copolymers, terpolymers and hydrophobically and/or hydrophilically modified and cross-linked derivatives of the above.

In certain embodiments the nano/micro particles can be dispersed in an aqueous or oleic medium depending upon the encapsulation matrix, and can contain one

or more soluble or dispersed oilfield production chemicals.

Modifications and improvements can be incorporated without departing from the scope of the invention.

Claims

1. A method of delivering a chemical to an oil or gas well, the method comprising associating the chemical with a carrier, and delivering the chemical and carrier to the well.

2. A method as claimed in claim 1, wherein the chemical is encapsulated by the carrier.

3. A method as claimed in any preceding claim, wherein the chemicals are released from the carrier upon contact with the produced fluids in the well.

4. A method as claimed in any preceding claim, wherein two or more chemicals are delivered via a single chemical injection conduit.

5. A method as claimed in claim 4, wherein the two chemicals are mutually incompatible.

6. A method as claimed in claim 4 or claim 5, wherein the two or more chemicals are released from the carrier at different locations in the well.

7. A method as claimed in any preceding claim, wherein the or each chemical is aggressive, insoluble or corrosive.

8. A method as claimed in any preceding claim, wherein the chemical and carrier are carried by a fluid to the desired point of delivery.

9. A method as claimed in claim 8, wherein the fluid phase carries a further chemical to be delivered to the well.

10. A method as claimed in claim 8 or claim 9, wherein the fluid is aqueous fluid.

11. A method as claimed in claim 8, or claim 9 wherein the fluid is oleic or organic fluid.

12. A method as claimed in any preceding claim, wherein the chemical-bearing carrier is injected at surface.

13. A method as claimed in any preceding claim, wherein the chemical-bearing carrier is injected at a wellhead.

14. A method as claimed in any preceding claim, wherein the chemical is selected from the group comprising scale inhibitors, corrosion inhibitors, wax inhibitors and dispersants, asphaltene inhibitors and dispersants, hydrate inhibitors, oxygen scavengers, pour-point modifiers, hydrogen sulphide scavengers, demulsifiers, biocides, gel breakers, tracers, friction reducers, surfactants, de-oilers and antifoaming agents.

15. A method as claimed in any preceding claim, wherein the carrier is associated with the chemical by a technique selected from the group comprising coacervation, interfacial polymerisation, desolvation, extrusion, agglomeration, emulsion polymerisation, gelation, chemical vapour deposition, fluid bed coating, spray drying and combinations thereof.

16. A method as claimed in any preceding claim, wherein the carrier is selected from the group comprising starch or flour, gum arabic, waxes, PVOH, polylactic acids, dextrins, low viscosity modified starches, arabinogalactan, gum acacia, casein, gelatin, carboxymethylcellulose, tragacanth, karaya, sodium alginate, tannin, and celluloses.

17. A method as claimed in any preceding claim, wherein the chemical is continuously delivered to the well.

18. A method as claimed in any preceding claim, wherein the carrier and chemical forms a particle.

19. A method as claimed in claim 18, wherein the particle size is in the range of 1μm-20μm.

20. A method as claimed in any preceding claim, wherein the carrier dissolves into the produced

fluids from the well after releasing the chemical.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/03547

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 E21B37/06 E21B43/25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 611 664 A (OSTERHOUDT III M GLENN ET AL) 16 September 1986 (1986-09-16) column 2, line 35 -column 3, line 13; claims 1,2,5-9,12-16 column 4, line 21 - line 49 ---	1-3,13, 14
X	US 4 986 354 A (CANTU LISA A ET AL) 22 January 1991 (1991-01-22) column 1, line 38 -column 4, line 2 --- -/--	1-3,8, 10-12, 14,15, 17-20

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 December 2001	12/12/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Boulon, A

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Interna Application No
PCT/GB 01/03547

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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